

# HIGH STRENGTH HOT CORROSION AND OXIDATION RESISTANT, DIRECTIONALLY SOLIDIFIED NICKEL BASE SUPERALLOY AND ARTICLES

## TECHNICAL FIELD

[001] The present invention relates to the field of nickel base superalloys for use in directionally solidified articles, and more particularly to such alloys providing articles having good mechanical properties at elevated temperatures, good resistance to hot corrosion, and good oxidation resistance.

## BACKGROUND OF THE INVENTION

[002] The increasing demands for efficiency in gas turbine engines have resulted in a demand for materials capable of withstanding more severe operating conditions. In particular, good strength is required for certain applications along with the resistance to hot corrosion, oxidation and creep.

[003] U.S. Pat. No. 3,619,182 describes a moderate strength superalloy, commercially known as IN 792, having purportedly superior corrosion resistance. The '182 patent describes an alloy having a composition, in weight percent, of: 9.5 - 14 Cr; 7 - 11 Co; 1 - 2.5 Mo; 3 - 4 W; 1 - 4 Ta; up to 1 Cb; 3 - 4 Al; 3 - 5 Ti; Al + Ti = 6.5 - 8; 0.005 - 0.05 B; 0.01 - 0.25 Zr; 0.02 - 0.25 C; bal. Ni. At the time the '182 application was filed, the alloy would have been cast to form an equiaxed (e.g., no indication of crystallographic orientation) article, e.g., for gas turbine engine components. The '182 patent is expressly incorporated herein by reference.

[004] An alloy, commonly known as GTD-111 which has been cast in equiaxed and directionally solidified forms. In equiaxed castings, GTD-111 has a nominal composition, in weight percent, of: 14 Cr; 9.7 Co; 1.5 Mo; 3.8 W; 3 Ta; 3 Al; 0.10 C; 5 Ti; 0.02 B; 0.04 Zr, bal. Ni. See, e.g., Schilke, et al. "Advanced Materials Propel Progress in Land-Based Gas Turbines", Advanced Materials and Processes, April 1992, page \_\_; see also, U.K. Patent GB 1,511,562 (13.7) 14.3 Cr; 9 - 10 Co; 1 - 1.5 Mo; 4.8 5.5 Ti; 2.8 - 3.2 Al; 3.7 - 4.3 W; 1 - 1.5 Nb; 2.5 - 3 Ta; 2.8 - 3.2 Al; 0.08 - 0.2 C; 4.8 5.5 Ti; 0.01 - 0.02 B; 0.02 - 0.1 Zr; and either 1.5 - 3.5 mixture of Ta, Cb and Hf, or 2.5 - 3 Ta or 2 - 2.5 Hf or 1 - 1.5 Cb [or Ta + Cb + Hf = 1.5 - 3.5]; and consisting of a matrix and a monocarbide phase distributed through the matrix consisting of: Ti, Mo, W and/or Ta and/or Cb and/or Hf in proportions such that the total of Mo and W is less than 15 weight percent of the carbide phase). In directionally solidified castings, the nominal composition is similar except for slightly lower amounts of zirconium. See, G.K. Bouse, "Eta ( $\eta$ ) and Platelet Phases in Investment Cast Superalloys", presented at Superalloys 1996, Seven Springs, PA.

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[005] U.S. Pat. No. 3,615,376 is directed to an alloy with a claimed composition, in weight percent, of: 0.15 - 0.3 C (described as more than is required for de-oxidation and sufficient to form grain boundary carbides); 13 - 15.6 Cr; 5 - 15 Co; 2.5 - 5 Mo; 3 - 6 W; 4 - 6 Ti; 2 - 4 Al; 0.005 - 0.02 Zr; balance Ni and incidental impurities; and also requires that Ti/Al be 1:1 - 3:1; Ti + Al between 7.5 - 9; Mo + 0.5W between 5 - 7; with a substantial absence of sigma phase and a stress rupture life of at least 25 hours at 27.5 ksi at 1800° F. A directionally solidified version of this alloy may also include a significant, intentionally added amount of Hf, e.g. up to or over 0.5 wt. %. It has been our experience generally that when adapting an alloy for columnar grain use, significant amounts of Hf must be added to an alloy, whether the starting alloy is equiaxed or single crystal, in order to provide critical properties, such as acceptable transverse ductility and to prevent hot tearing during casting, required for uses such as gas turbine engine components.

[006] The alloy disclosed in commonly owned U.S. Pat. No. 4,597,809 arose from an investigation of the effects of the minor elements carbon, boron, zirconium and hafnium on the properties of certain commercial alloys in single crystal form (the major function of these minor elements appeared to involve grain boundary strengthening). It was previously determined that fabrication of alloy IN 792 (originally in equiaxed form) as altered in the '182 patent in single crystal form - but without grain boundary strengtheners - provided substantial and unexpected benefits in mechanical properties. The single crystal IN 792 articles evaluated had no intentional additions of carbon, boron, zirconium or hafnium. In the course of the investigation of the effects of the minor elements on IN 792, it was observed that adding small amounts of carbon, i.e. 0.10 wt. % to IN 792 single crystals substantially improved the hot corrosion resistance but at the same time substantially reduced the mechanical properties of the material. The improvement of the hot corrosion resistance was completely unexpected and was not understood. As a further step in the investigation, additions of tantalum were made to the basic IN 792 composition in coordination with the added carbon and it was found that when the added tantalum and carbon contents were balanced (to tie up the carbon as tantalum carbide) a good combination of improved mechanical properties and improved corrosion resistance resulted.

[007] Single crystal articles are in many cases more difficult and expensive to produce, relative to their columnar grain counterparts, especially as component size increases. Moreover, where relatively large articles are to be produced, e.g., for land based gas turbine applications, the difficulty and expense can increase substantially.

[008] As noted above, when adapting an alloy originally designed for use in single crystal articles for use in columnar grain directionally solidified applications, or adapting an alloy originally designed for use in equiaxed form for use as columnar grain directionally solidified applications, certain compositional changes are typically warranted to increase grain boundary strength and ductility. For example, hafnium, carbon, boron and zirconium are typically added to the single crystal or equiaxed

composition for the purpose of improving properties, such as transverse creep strength and/or ductility. However, adding hafnium, even in small amounts such as 0.5 - 2 wt. % has several undesirable consequences including increased segregation banding, which can significantly reduce castability of the alloy. In addition, hafnium promotes increased eutectic  $\gamma/\gamma'$  formation.

[009] Hafnium also lowers the incipient melting temperature of the alloy, thereby reducing the temperature range or window available for a solution heat treatment of the alloy. Since achieving good creep strength typically requires subjecting the part to a suitable solution heat treatment, the reduced window makes it more difficult - in some cases not possible - to provide a suitable solution heat treatment. This problem is exacerbated with larger articles, such as land based gas turbine components where segregation becomes worse. Adding hafnium also increases density of the alloy, increasing the weight of parts fabricated from the alloy, and also can reduce the microstructural stability of the alloy.

[010] It would be desirable to provide a material for the fabrication of columnar grain articles, and to provide such articles, which have adequate strength relative to comparable articles in single crystal form, and which also demonstrate at least comparable oxidation and corrosion resistance.

[011] It would also be desirable to provide the benefits of an alloy composition adapted for use as in columnar grain directionally-solidified parts while maintaining the benefits of the alloy as adapted for use in single crystal articles.

[012] It would likewise be desirable to provide such an alloy which provides oxidation resistance in columnar grain form at least comparable to that in single crystal form.

[013] It would be further desirable to provide such an alloy that provides adequate transverse ductility without the addition of hafnium.

[014] It would be yet further desirable to provide such an alloy which does not require a solution heat treatment in order to achieve adequate creep strength.

#### SUMMARY OF THE INVENTION

[015] Alloys for columnar grain directionally solidified articles are disclosed which have at least comparable oxidation resistance relative to single crystal counterparts, and corrosion resistance at least comparable to such alloys. Moreover the inventive alloys have oxidation resistance at least equal to equiaxed counterparts, and at least equal corrosion resistance. In many instances, the alloys of the present invention provide articles in columnar grain directionally solidified form with superior oxidation resistance than comparable articles and alloys in equiaxed or single crystal form.

[016] The inventive alloys comprise a matrix with a general composition, in weight percent, of 10 - 14.5% chromium; 8 - 10% cobalt; 1.25 - 2.5% molybdenum; 3.25 - 4.25% tungsten; 4.5 - 6% tantalum; 3.25 - 4.5% aluminum; 3 - 5% titanium; 0.0025 - 0.025% boron; up to about 0.02% zirconium (no

intentional additions); 0.05 - 0.15% carbon; and having no intentional addition of niobium; no intentional addition of hafnium; and balance essentially nickel; wherein aluminum + titanium is between about 6.5 - 8%. The alloy also includes roughly about 0.4 to 1.5 vol. % of a phase based on tantalum carbide.

[017] In columnar grain form, the alloy exhibits oxidation resistance at 2000° F of at least roughly 2.5X, creep rupture life at 1400° F of at least roughly 2.4X and at 1800° F of at least roughly 1.5X compared to a similar article having a nominal composition of 14 Cr, 4.9 Ti, 1.5 Mo, 3.8 W, 2.8 Ta, 3 Al, 9.5 Co, 0.01 B, 0.02 Zr, 0.1 C, and balance Ni.

[018] The invention composition may be cast in columnar grain, directionally-solidified (or single crystal) form according to the teachings of various prior patents as is known in the art. Typically the grains of the casting will have an orientation parallel to the principal stress axis of the component, e.g.,  $\langle 100 \rangle$  although deviations may be tolerated. In the case of single crystal article, we believe that the articles can include high angles boundaries of up to and in excess of 20°. Where needed, the present composition after being cast in directionally solidified form can be heat treated in order to improve the mechanical properties of the alloy by controlling the gamma prime particle size in accordance, e.g., with the teachings of U.S. Pat. No. 4,116,723 which is also expressly incorporated herein by reference. However, such articles as cast may have adequate creep strength (depending upon their intended use) such that solution heat treatment is unnecessary.

[019] Other features and advantages will be apparent from the specification and claims which illustrate an embodiment of the invention.

#### BRIEF DESCRIPTION OF DRAWINGS

[020] FIG. 1 is a graph illustrating preferred amounts of carbon and boron in accordance with the present invention.

[021] FIG. 2 is a graph illustrating the relative hot corrosion resistance of the inventive alloy.

[022] FIG. 3 is a graph illustrating the relative oxidation resistance of the inventive alloy.

[023] FIGS. 4, 5 and 6 are graphs illustrating the creep rupture life of several variations of the inventive alloy.

[024] FIG. 7 is a graph illustrating transverse creep ductility of the inventive alloy.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[025] The present invention is based on altering the chemistry originally adapted for use in single crystal articles, e.g., commonly owned U.S. Pat. No. 4,597,809 which is expressly incorporated by

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reference herein, into an alloy that is particularly useful in the production of columnar grain articles - although we believe that the alloy of the present invention may also be useful in the production of single crystal articles also. In columnar grain form, cast articles in accordance with the present invention are characterized by good hot corrosion resistance, good oxidation resistance, and good longitudinal and transverse creep-rupture properties. We also considered the composition of an alloy generally designated "GTD-111", see, e.g., GB Pat. No. 1,511,652, which is used in equiaxed and columnar grain forms, and has a nominal composition in weight percent of 14 Cr, 4.9 Ti, 1.5 Mo, 3.8 W, 2.8 Ta, 3 Al, 9.5 Co, 0.01 B, ~0.02 Zr, ~0.05 C, and balance Ni. We believe that beneficial and different properties may be achieved, among other things, by altering the composition of the single crystal '809 alloy by significantly increasing the carbon and boron levels (and allowing a maximum amount of zirconium in the alloy) on one hand, or by altering the nominal content of the equiaxed/columnar grain -111 alloy by significantly increasing tantalum, aluminum, molybdenum and boron contents, and significantly decreasing the titanium and chromium contents on the other hand (e.g., the '562 patent teaches among other things high chromium (above 13.7 wt. %); relatively higher cobalt (over 9.5 wt. %); that more than 0.02% zirconium is acceptable; and that tantalum over 3 - 3.5 wt. % will cause unacceptable microstructural instability). This is particularly true in the case of columnar grain articles, together with close control of the overall composition.

[026] The generally preferred composition of the present invention consists essentially of, in weight percent, about 10 - 14.5% chromium; 8 - 10% cobalt; 1.25 - 2.5% molybdenum; 3.25 - 4.25% tungsten; 4.5 - 6% tantalum; 3.25 - 4.5% aluminum; 3 - 5% titanium; 0.0025 - 0.025% boron; up to about 0.02% zirconium; 0.05 - 0.15% carbon; and having no intentional addition of niobium; no intentional addition of hafnium; and balance essentially nickel; wherein aluminum + titanium is between about 6.5 - 8%. The alloy also includes roughly about 0.4 to 1.5 vol. % of a phase based on tantalum carbide. More preferably, the alloy comprises about 11- 13% chromium; 8.25 - 9.75% cobalt; 1.5 - 2.25% molybdenum; 3.4 - 4.3% tungsten; 4.7 - 5.5% tantalum; 3.3 - 4% aluminum; 3.75 - 4.3% titanium; 0.008 - 0.025% boron; up to about 0.02% zirconium; 0.08 - 0.13 carbon; wherein aluminum + titanium is between about 7 - 8%. Most preferably, the alloy comprises about 12% chromium; 9% cobalt; 1.9% molybdenum; 3.8% tungsten; 5% tantalum; 3.6% aluminum; 4.1% titanium; 0.015% boron; less than 0.02% zirconium; 0.10% carbon; and having no intentional addition of zirconium (any in any event less than about 0.02 Zr) and no intentional addition of niobium; no intentional addition of hafnium; balance essentially nickel.

[027] We discovered that even small additions of zirconium detrimentally affected the castability of part, particularly large parts such as land based gas turbine engine blades. Articles having more than about 0.02 wt. % zirconium tended to tear after on investment casting, during cooling and solidification of the molten material. While not fully understood, the tearing problem was obviated

where zirconium was present in less than about 0.02 wt. percent. Accordingly, the inventive composition includes no intentional additions of zirconium, and whether or not it is practical to tolerate about up to about 0.02 wt. %, we prefer less. In an effort to improve the tearing problem, we tried several compositions, including intentional additions of up to about 1.0 weight % hafnium which did not obviate the problem, and would be expected to increase the weight of the alloy and decrease the incipient melting temperature of the alloy. Such a result would also restrict the available temperature window for solution heat treatment of articles, particularly larger articles such as land based gas turbine components. Accordingly, we prefer that the alloy and articles also include no intentional addition of hafnium.

[028] A number of modifications ("Mod") were prepared by investment casting columnar grain articles, and were evaluated as described below. Some of the compositions (all in wt. %) are outside of the preferred ranges invention, but are still encompassed by the invention. Overall, the composition of Mod 4 is the preferred composition of the six listed below, but the other Mods and other compositions within the inventive ranges are also useful. In each case, the balance of the composition comprises nickel and small amounts of incidental impurities. For example, we have optimized the alloy for castability, without debiting other properties, by increasing carbon to about 0.08 wt. % and increasing boron to about 0.015 wt. %. The optimization effort was brought about, in part, by significant hot tearing during casting of large parts. The tearing was reduced and eliminated as carbon levels were raised up to at least about 0.08 wt. %. We were surprised that the tearing problem was largely eliminated at the carbon levels were raised from about 0.07 to 0.08 w. %.

Alloy	Cr	Ti	Mo	W	Ta	Al	Co	B	Zr	C	Hf
GTD 111	(14)	(4.9)	1.5	3.8	(2.8)	(3)	9.5	0.01	0.02	0.1	0
4,597,809	12.2	4.2	1.9	3.8	5	3.6	9	0	0	0.07	0
Mod1	11.56	4.03	1.84	3.75	5.1	3.55	8.9	0.005	0.014	0.07	0.49
Mod2	11.68	4.04	1.83	3.72	4.96	3.58	8.86	0.005	0.015	0.06	0.88
Mod3	12.25	4.01	1.83	3.69	5.01	3.5	8.82	0.018	0.091	0.11	0.48
Mod4	11.94	4.03	1.84	3.75	5.15	3.55	8.93	0.008	0.02	0.06	0.01
Mod5	11.61	4.05	1.84	3.74	5.29	3.57	8.89	0.008	0.032	0.07	0.49
Mod6	11.9	4	1.82	3.7	4.93	3.52	8.79	0.019	0.103	0.12	0.94

The articles to be evaluated were investment cast, and then given similar heat treatments - a solution heat treat at about 2050° F for 2 hours, followed by precipitation heat treat at 1975 F for 4 hours, followed by stabilization heat treat at about 1550° F for 24 hours. In some cases, articles were solution heat treated at 2150 - 2200° F for less time, but showed no significant increase in properties.

[029] FIG. 2 shows the relative hot corrosion resistance of the inventive alloy compared to other alloys, including the -111 alloy. Corrosion testing was performed at 1650° F. in a corrosion gaseous environment produced by combustion of Jet A fuel (30:1 air fuel ratio) with addition of 20 ppm of

ASTM sea salt and sufficient sulfur dioxide to produce a sulfur content equivalent to a 1.3% S content in the fuel. The numbers presented are the hours of exposure required to produce 1 mil of corrosive attack. As seen in the FIG., the inventive alloy exhibits corrosion resistance comparable to GTD-111 and significantly better than single crystal alloys of similar compositions, see, commonly owned U.S. Pat. Nos. 4,209,348 and 4,719,080 both of which are expressly incorporated by reference herein.

[030] FIG. 3 shows the relative uncoated, burner rig oxidation resistance of several Mods of the inventive alloy at 2000° F and several other alloys. While the oxidation resistance exceeds the oxidation resistance of GTD-111, Mod 4 is significantly higher (at least 2.5X) and similar to the oxidation resistance of the single crystal alloy of the '809 patent. The increase in aluminum content and decrease in titanium content if the inventive alloy over GTD-111 is largely responsible for the inventive alloy's greater oxidation resistance.

[031] The time to produce 1% creep was tested (in many cases both transverse and longitudinal) in specimens at 1400° F with an applied stress of 85 ksi and at 1800° F with an applied stress of 27 ksi. The results are illustrated in FIGS. 4, 5 and 6. Again, the inventive alloy exhibited creep rupture lives exceeding the -111 alloy.

[032] Transverse creep rupture ductility was also tested for several Mods, as shown in FIG. 7. Minimum elongation at rupture (see FIG. 4) was at least about 5%. Such transverse ductility would be expected to provide a material that is more resistant to the formation of casting cracks.

[033] In sum, the present invention is either based on a modification of a published composition for a prior art columnar grain article, or of a published composition for a prior art single crystal article. Using the prior art columnar grain article, the present invention includes among other things significantly increasing tantalum, aluminum and molybdenum contents, and significantly decreasing the titanium and chromium contents. Using the prior art single crystal article, the present invention includes among other things discreet amounts of boron and carbon while controlling the presence of zirconium (each of which are explicitly kept out of the prior art alloy). In any event, the inventive alloy and articles fabricated from the alloy exhibit a good combination of oxidation resistance, corrosion resistance and creep-rupture resistance at various temperatures.

[034] It should be understood that the invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the spirit and scope of this novel concept as defined by the following claims.

[035] We claim: